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VALIDATION OF GLASS FORMATION AND CRYSTALLIZATION PROCESSES FOR MULTICOMPONENT SYSTEMS FROM THE STANDPOINT OF THE ACID-BASE CONCEPT OF SILICATE MELTS

A. M. Kondyurin,¹ M. V. Tamazov,¹ and I. G. Dovzhenko^{1,2}

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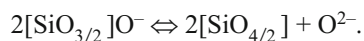
Glass formation and crystallization of melts in the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{SiO}_2-\text{MnO}_2$ with different Fe_2O_3 content are studied. A mechanism is proposed for the crystallization of glass from the standpoint of the acid-base concept of silicate melts. The role of aluminum and iron ions as glass formers of the elemental-oxygen framework or as modifiers as a result of the displacement of acid-base equilibria with a change of the iron oxide content is shown.

Key words: acid-base concept, silicate melt, glass formation, crystalline phase.

Our current understanding of the chemical nature of oxide glass-forming melts was developed on the basis of an approach toward examining their structure and construction as products of the displacement of a series of chemical and structural equilibria [1]. The most important equilibria of this type are acid-base equilibria reflecting dissociation processes in the anionic framework of oxide melt.

M. M. Shul'ts's acid-base concept treats all oxide melts as dissociated substances capable of detaching or attaching in the process of acid-base transformations of an oxygen ion O^{2-} , so-called dissociated oxygen [1]. Here, the rupture of one bridge elemental-oxygen bond should be regarded as a single act of the acid-base process. Any atom can be regarded as a product of interaction of an acid, i.e., a positively charged atomic nucleus, and a base — a negatively charged electron cloud for all elements in the periodic system. Thus, the chemical inertness of a substance is determined by its energy state and structural completeness.

The quantitative relation and type of chemical-structural groupings forming the anionic framework of the melt is determined by its chemical composition and determines the set of acid-base equilibria which are possible in a melt at constant temperature. The acid-base processes occurring in melts are characterized by dissociation with these groupings participating and can be described by the equilibrium reaction



The aim of the present work is to investigate glass formation and crystallization of glasses in the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{SiO}_2-\text{MnO}_2$ depending on the content of iron (III) oxide and to analyze the experimental data obtained from the standpoint of the acid-base concept.

Chemical Composition of the Base Glass Batch (wt.%)^{*}

SiO_2	40.0
Al_2O_3	19.5
CaO	20.3
MgO	4.0
Na_2O	8.2
K_2O	5.6
MnO_2	2.4

A base glass batch was used for the experiments.

The content of iron (III) oxide introduced into glass batch above 100% was varied from 8 to 20%. The glass batches Nos. 1, 2, 3 and 4 with 8, 12, 16 and 20% Fe_2O_3 , respectively, were melted at temperature 1250°C. The glasses obtained were dark brown. The glass made using composition No. 4 with 20% Fe_2O_3 spontaneously crystallizes when cooled in air, so that it was excluded from subsequent studies.

Differential-thermal analysis (DTA) was used to study the crystallization capacity and temperature intervals of

¹ South-Russian State Technical University – Novocherkassk Polytechnical Institute, Novocherkassk, Russia.

² E-mail: dovz-ig@yandex.ru.

^{*} Here and below the content by weight, %.

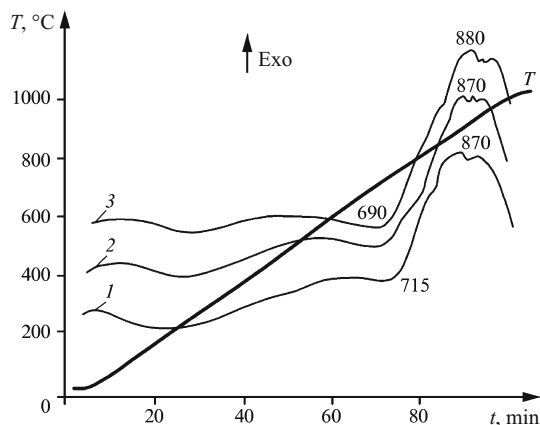


Fig. 1. Thermograms of the glasses. The numbers on the curves denote the glass compositions.

phase transitions of glasses Nos. 1, 2 and 3. Thermograms of the experimental glasses are displayed in Fig. 1.

Endothermal effects are observed in the DTA curves in the temperature interval 680 – 715°C and exoeffects in the interval 850 – 890°C. In addition, the endo- and exoeffects in different glasses manifest at close temperatures. However, as the Fe_2O_3 content in the glasses increases the intensity of the exoeffects increases due to higher heat release accompanying the formation of crystalline phases and could be due to an increase of the degree to which the glasses are crystallized. The character of the DTA curves showed that for the experimental compositions of the glass batches an endothermal effect is observed at temperatures 690°C for glasses Nos. 1 and 2 and 715°C for glass No. 3. To study the possibility of obtaining glass matrices for heat-resistant coatings with sital-type structure they were subjected to two-step heat-treatment at the temperatures 715 and 890°C, found by the DTA method, with isothermal soaking for 2 h.

The glasses heat-treated at the indicated temperatures were studied by x-ray phase analysis. No distinct peaks corresponding to crystalline phases were found in the x-ray diffraction patterns at 715°C. The presence of weak peaks can only indicate the initial stage of crystallization. Peaks corresponding to gehlenite (0.371, 0.285, 0.243, 0.192 nm) and melilite-like solid solutions (0.307, 0.232, 0.185, 0.140 nm) with an okermanite iron-containing component were identified at 890°C. The intensity of the gehlenite peaks increases with increasing Fe_2O_3 content, which likewise could be an indication of an increase in the degree to which the glasses are crystallized.

To study the effect of iron oxide on crystallization studies were performed to determine the viscosity of the experimental glasses for the temperatures at which the crystalline phases are formed.

The temperature behavior of the curves showing the viscosity of the glasses as a function of the Fe_2O_3 content is shown in Fig. 2. As temperature increases, the viscosity of

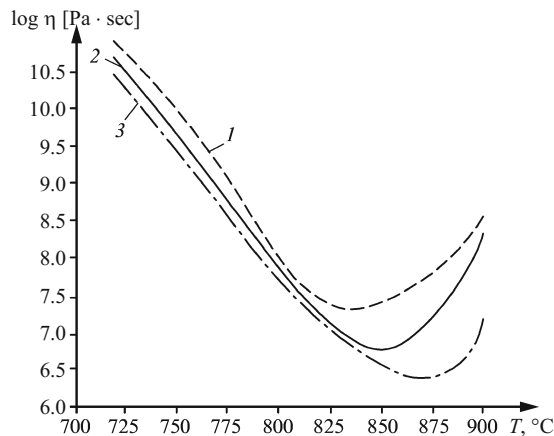


Fig. 2. Viscosity of the glasses versus the Fe_2O_3 content: 1) 8% Fe_2O_3 in the glass; 2) same, 12%; 3) same, 16%.

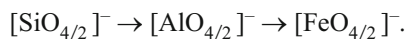
the glasses first decreases and then increases, attesting to their crystallization. In addition, crystallization occurs at temperatures 879 – 893°C. This viscosity of the glasses decreases with increasing Fe_2O_3 content. This agrees well with studies of the effect of Fe_2O_3 on the viscosity of enamels and with the data presented in [2].

Iron oxide acts as a modifier, breaking the elemental-oxygen network of the glass. The total amount of modifiers increases with the Fe_2O_3 content in the experimental glasses. The number of breaks in the elemental-oxygen network increases with increasing temperature; thus, glasses with high Fe_2O_3 content have lower viscosity at the same temperatures. As Fe_2O_3 content increases the inflections in the temperature curves of the viscosity become smoother, showing that the temperature interval of crystallization and the degree of crystallization of the glasses increase. Analysis of the temperature behavior of the viscosity curves shows that the coating based on glass No. 3 exhibits a wider firing interval, as a result of which this glass is of greater practical value for synthesizing heat-resistant glass ceramic coatings.

According to the acid-base concept glass formation and crystallization in the multicomponent system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{SiO}_2-\text{MnO}_2$ can be described as follows. Silica forms a framework of silicon-oxygen tetrahedra in silicate glasses. Aluminum and iron oxides become integrated into the glass network in the form of a corresponding polyhedron and are network formers. In contrast to network-forming oxides the modifying oxides do not participate in building a glass network — they break the network. Elemental-oxygen polyhedra are formed according to the principle of the construction of complex compounds with the participation of the oxide in alkali-metal oxides; the alkali-oxide cation neutralizes the excess negative charge of the polyhedron [3].

It is known that for $([\text{Al}_2\text{O}_3] + [\text{Fe}_2\text{O}_3])/([\text{MeO}] + [\text{Me}_2\text{O}]) < 1$ the Al^{3+} and Fe^{3+} ions are network formers [4]. In this case, some Al^{3+} and Fe^{3+} ions stabilize in four-fold

coordination, which is optimal for forming a network with irregular displacement of bonds. The elements can be arranged in the following series according to the decrease of their capability to form tetrahedral coordination (or to be network formers):



The fact that Al^{3+} and Fe^{3+} are in four-fold coordination imparts great freedom in the distribution of bonds for oxygen ions in the glass structure. Though it does not preclude the possibility of network forming the six-fold coordination of these ions with respect to oxygen makes the network structure more ordered, which subsequently facilitates the crystallization of such melts [5]. Thus, the anionic matrix of glass melts in the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{SiO}_2-\text{MnO}_2$ can be represented as consisting of the following groupings:

$[\text{SiO}_{4/2}]^-$ — silicon-oxygen tetrahedra with bridge oxygens;

$[\text{SiO}_{3/2}]^+$ — silicon-oxygen positively charged groupings (tetrahedra with oxygen vacancy);

$([\text{SiO}_{3/2}]\text{O}^-)_m M^{n+}$ — the M^{n+} ion is a modifier bound with bridge and non-bridge oxygens, where M^{n+} represents Na, K, Ca, Mg, Al, Fe and Mn ions;

$[\text{RO}_{4/2}]M^{n+}$ — element-oxygen grouping acting as a network former, where R denotes Al and Fe atoms and M denotes Na, K, Ca, Mg and Mn ions;

O^{2-} — dissociated oxygen ion.

The glasses formed when the melt is supercooled consists of the following groupings: $[\text{SiO}_{4/2}]^-$, $([\text{SiO}_{3/2}]\text{O}^-)_m M^{n+}$ and $[\text{RO}_{4/2}]M^{n+}$. Free M^{n+} and O^{2-} ions can also be present in small amounts.

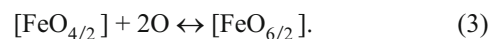
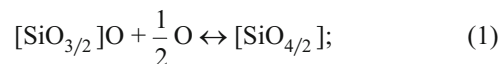
The following mechanism of crystallization of glass matrices can be proposed on the basis of the experimental data.

The acid-base interaction in the experimental glasses can be viewed as a striving to level the energy disparity between the bonds of structural elements and switch by means of crystallization or structural change of the elemental-oxygen framework into a compound with more perfect and energetically more stable structure. The structure of the glass matrices studied can be viewed as a dynamical structural model with energetically disparate ionic-covalent bonds between the coordination groups and individual structural elements, which cause their micro-non-uniformity [6].

As the Fe_2O_3 content increases, the ratio of bridge and non-bridge bonds between the elements of network formers and oxygen changes in the structure of glass matrices, as a result of which ions acquire diffusion mobility and, correspondingly, the short- and long-range order in the arrangement of tetrahedral groups changes. At the first step of heat-treatment of glasses at temperature 690 – 715°C a process of phase differentiation of the elemental-oxygen framework of glass matrices with a decrease of viscosity occurs as a result of the energy disparity between the bonds in the structural

groupings. As the bonds of the elemental-oxygen framework become redistributed micro-non-uniform regions form in it because of the different diffusion mobility of Al^{3+} and Fe^{3+} ions; in one such region aside from the groupings $[\text{SiO}_{4/2}]^-$, $([\text{SiO}_{3/2}]\text{O}^-)_m M^{n+}$ the groupings $[\text{AlO}_{4/2}]M^{n+}$ predominate and in another $[\text{FeO}_{4/2}]M^{n+}$ predominate. The Al^{3+} and Fe^{3+} ions in these groupings are network formers [3].

The following acid-base reactions can occur in the process of phase differentiation of the elemental-oxygen framework during heat treatment:



The reaction (1) is due to the effect of modifier ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+}). The reactions (2) and (3) can compensate one another, showing the role of aluminum and iron ions either as modifiers of the elemental-oxygen framework or as network formers in accordance with the scheme $[\text{AlO}_{6/2}] + [\text{FeO}_{4/2}] \leftrightarrow [\text{AlO}_{4/2}] + [\text{FeO}_{6/2}]$.

For constant ratios of other components and increasing Fe_2O_3 content in glasses the equilibrium shifts in the direction of stabilization of Al^{3+} ions as network formers while iron ions stabilize as modifiers, since the total number of modifier ions increases and the degree of connectedness of the elemental-oxygen framework decreases.

At the second heat-treatment step for glasses at temperature 890°C, the conditions required for the formation of energetically more stable structure are created as a result of a decrease of viscosity and, correspondingly, increase of the diffusion mobility of ionic associates and ions. This is indicated by x-ray diffraction data. In a region of phase differentiation with the groupings $[\text{SiO}_{4/2}]^-$ and $[\text{AlO}_{4/2}]M^{n+}$ crystallization of silicates of the gehlenite type and melilite-like solid solutions occurs. In this case the structural groupings $[\text{AlO}_{4/2}]M^{n+}$ together with the groupings $[\text{SiO}_{4/2}]^-$ play the role of the structural elements of short-range order of the crystalline phases formed.

Gehlenite possesses cubic structure. In the crystalline phase aluminum is in four-fold and iron six-fold coordination, the latter becoming embedded between crystal lattice sites. Especially important is the fact that silicon and aluminum are mutually interchangeable in the glass-forming network and in crystalline silicates. According to [3] Al occupies Si sites in the $[\text{SiO}_{4/2}]^-$ tetrahedra in melilite-group minerals. At the completion of the crystallization process the main groupings present in the residual glass phase are $[\text{SiO}_{4/2}]^-$, $[\text{FeO}_{4/2}]M^{n+}$, $[\text{AlO}_{4/2}]M^{n+}$ and $[\text{AlO}_{6/2}]$. In the glass phase the Fe^{3+} ions, being network-formers together with the ions Si^{4+} , manifest acid properties while the Al^{3+} ions, being modifiers, exhibit basic properties.

In summary, the crystallization of glasses in the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{SiO}_2-\text{MnO}_2$ occurs as a result of phase differentiation of the elemental-oxygen framework of the glass matrix, which from the standpoint of the acid-base concept of the structure of silicate melts can be described by acid-base equilibrium reactions, showing the role of Al^{3+} and Fe^{3+} ions either as glass-formers of the elemental-oxygen framework or as modifiers. An increase of the iron (III) oxide content in the experimental glasses affects the shift of the acid-base equilibrium toward formation of the groupings $[\text{AlO}_{4/2}]^+$, which together with $[\text{SiO}_{4/2}]^+$ groupings with constant ratios of the other components form fragments of the elemental-oxygen framework; the composition of the fragments is close to that of gehlenite and melilite-like solid solutions.

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